

# Methodological Aspects of Assessment of Potential Toxic Pollution of Hydrosphere and Environment by Mining Industry Objects

Igor' V. Kemkin \*<sup>a, b</sup>, Raisa A. Kemkina<sup>a, b</sup>

a - Far East Federal University, 690950, Vladivostok, Soukhanova Street, 8, Russia

b - Far East Geological Institute, Far Eastern Branch of Russian Academy of Sciences, 690022, Vladivostok, prospect 100-letiya Vladivostoka, 159, Russia

kemkin@fegi.ru

## Abstract

The article discusses questions related to the integrated use of mineralogical-geochemical research methods of ore deposits under exploration and mathematical modeling of behavior of ore minerals in the hypogene zone for qualitative and quantitative assessment of potential ecological threat of pollution by toxic elements, that is one aspect of reducing risk of technogenic disasters related to the mining activities of human.

## Keywords

Toxic Pollution; Tailings Dam; Ore Minerals; Computer Modeling.

## Introduction

The specificity of mining of ore deposits is that the final (marketable) product when extracting three or four useful components takes about 10-20% of all ore mass mined (e.g., Trubetskoy and Galchenko, 2002). Larger part of the ore mass mined with significant concentrations of various ore-forming chemical elements, including toxic, are accumulated in the form of waste of ore-dressing (so-called "tails") placed in special facility called tailings dam. Obviously, that the unclaimed portion of ore material being extracted to the earth surface as a result of hypogene processes (weathering) undergoes oxidation, dissolution, transformation to other mineral forms and aqueous solutions that significantly affects the environment in the mine adjacent areas (e.g., Jushkin and Pavlishin, 1991). This is due to at least two reasons. Firstly, extraction and warehousing at the ground surface fine-crushed ore-rock mass increase natural oxidants access to ore minerals (e.g., water, oxygen, carbon dioxide, bacteria, etc.). Secondly, area of interaction of oxidants in tailings dam orders of magnitude are higher than in natural ore bodies. All these together

significantly accelerate processes of oxidation, dissolution, hydration of ore-rock mass and promote carryover into the environment a large number of different chemical elements, including toxic in the form of aqueous solutions. In this connection, studies on evaluation and prediction of potential ecological threat of warehoused wastes of ore-dressing are highly relevant, as ultimately aiming at the preservation of ecological balance in nature and creation of safe living conditions.

## Methods

Undoubtedly that the mineralogical investigations (i.e. detailed study of the material constitution of ores) even at the early stages of study of ore deposit may help to identify the most important quality characteristics and technological parameters of ores (which is important for the choice of mining operations technology and ore-dressing), as well as range of the potential toxic elements contained in them. Thus, having executed complex of mineralogical and geochemical research of ore material, even at the stage of ore deposit exploration, (before passing it to commercial development) it is possible to determine composition of potential ecologically hazardous elements contained in its ores. Knowing the main industrial component of ores, it is possible to qualitatively estimate which toxic elements will be concentrated in tailings dam.

For quantitative assessment of ecological hazard of the unclaimed ore mass, it is necessary to clarify geochemical behavior of ore minerals in hypogene conditions in compliance with climate conditions where tails are warehoused. If ore deposits under development, and waste of ore-dressing are located in tailings dam, this problem can be solved by detailed

mineralogical and geochemical investigations of hypogene (secondary) minerals that form in the tails bulk. The further comparison of chemical compositions data of hypogene (primary) and hypogene minerals will show which chemical elements have migrated from technogenic system into the environment. In addition, geochemical analysis of drainage water stemming from tailings dam allows to establish composition, ionic forms and concentration of toxic elements migrating to the environment.

For ore deposits that are in the exploration stage, this problem can be successfully solved by using mathematical modeling of physicochemical processes of transformation of a primary ore minerals based on thermodynamic calculations of mineral-forming processes in subsurface (hypogene zone) system, tending to physical-chemical equilibrium. It is known that during formation of ore bodies within the rock masses, an isolated equilibrium system is formed in which all chemical elements are bounded into mineral phases, i.e., their mobility is extremely low. However, equilibrium of system is impaired when ore-rock mass is moved to the hypogene zone where it undergoes oxidation, dissolution, hydration and hydrolysis as results of interaction with atmosphere, water, microorganisms, and some other oxidants. In this case, the system tends to equilibrium again due to transition of some elements into aqueous solution in the form of various ions, and crystallization of new mineral phases.

One means of mathematical modeling is the computer software "Selector-Windows" developed by I.K. Karpov, K.V. Chudnenko, and V.A. Bychinskii (Karpov et al., 1976; Karpov, 1981). The software "Selector-Windows" does not calculate chemical reactions. It finds the global minimum of a thermodynamic potential (i.e., minimum of the Gibbs free energy) and determines mineral paragenesis on this basis. The Gibbs energy minimization method implies both the equilibrium aqueous solution with its components and minerals falling out of it, equilibrium of aqueous solution and its components and minerals with a primary rock-mineral mass. This method does not require additional costs because clarification of mineralogical and chemical composition of ores is an essential part of studying of any ore deposit that is needed for calculation of useful mineral reserves, and for choice of mining technology, ore-dressing, and etc. Using this method will allow to define a productive technologies of ore extraction and ore-dressing before starting commercial production of deposit and also

competently develop a set of effective environmental protection measures reducing a degree of negative impacts on the environment. Efficiency of this method can be demonstrated on an example of the Prasolovka gold deposit.

## **Result and Discussion**

According to the data of mineralogical and geochemical study (e.g., Kemkina and Kemkin, 2007), the Prasolovka gold deposit ores are represented by native metals and intermetallic, tellurides, selenides, sulfides and sulfosalts of Cu, Pb, Ag, Bi. The main ore minerals are as following: native gold, silver, tellurium, pyrite, marcasite, chalcopyrite, galena, acanthite, proustite, calaverite, krennerite, sylvanite, clauthallite, naumannite, roquesite, different-composition tennantite-tetrahedrite-goldfieldite fahlores and others, total amount of which comes nearer to 50. These minerals comprise 15 chemical elements - Zn, Pb, Cu, Mo, Fe, As, Sb, In, Bi, Cd, Te, Se, S, Ag, Au, and only 2 of them (Ag and Au) are not toxic. Concentrations of these elements vary considerably in different minerals, which is caused by a form of their occurrence into the crystal lattices of ore minerals - mineral-forming or isomorphic. The contents of these elements are as following (in wt %): As - 0.13-18.00, Pb - 0.09-84.43, In - 48.24, Cd - 0.01-0.42, Te - 0.01-99.85, Zn - 0.01-64.77, Cu - 0.01-77.45, Fe - 0.05-46.48, Se - 0.01-50.04, Sb - 0.01-25.32, Bi - 0.02-52.83. However, according to technical and economic requirements, the total content of each of above elements are not sufficient for integrated mining operations. Only minerals and mineral phases of Au and Ag represent the main industrial components for the Prasolovka deposit. Consequently, the ore minerals not containing these elements will fall into the tailings dam. Obviously, that unclaimed ore materials which have been extracted and located at the ground surface will represent a serious ecological threat to local hydrosphere and the environment as a whole.

For purpose of qualitative and quantitative assessment of potential ecological pollution of area adjacent to the Prasolovka deposit, the modeling of physicochemical processes of transformation for most common ore minerals has been executed. Two variants of tasks were considered during modeling - geochemical behavior of individual mineral in interaction with natural waters and atmosphere, as well as all their totality in order to determine the potential ecological hazard of an individual mineral and, accordingly, their all natural association. All models were chosen

uniform thermo-barometric conditions -  $T = 25^{\circ}\text{C}$  and  $P = 1 \text{ atm}$ . The composition of rainwater is adopted in accordance with (Karpov, 1981) -  $\text{N}_3^-$ ,  $\text{N}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{NH}_4\text{N}_3^-$ ,  $\text{HNO}_2^-$ ,  $\text{NH}_4\text{NO}_3^-$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{Ar}$ ,  $\text{He}$ ,  $\text{Kr}$ ,  $\text{Ne}$ ,  $\text{OH}^-$ ,  $\text{H}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{pH} = 5.66$ . Atmosphere composition according R. Horne (1972) is as following -  $\text{N}_2 - 53.9478$ ,  $\text{O}_2 - 14.4847$ ,  $\text{C}_2\text{H}_6 - 0.0104$ ,  $\text{Ar} - 0.3209$  (mol/kg).

The results of modeling show that being individual mineral or all mineral association, a large number of toxic metals come into aqueous solution. In case of oxidation of sulfides, for example, 1 mole of cadmium-copper-containing sphalerite (97 g of  $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Cd}_{0.01}\text{S}_{1.03}$ ) in 1 ton of water, contained in equilibrium with the atmosphere, this mineral is completely dissolved forming 258.76 g of new mineral phase  $\text{ZnSO}_4(\text{H}_2\text{O})_6$  (biankite). The remaining portion of the original mineral transforms into cations  $\text{Cd}^{+2}$ ,  $\text{CdO}$ ,  $\text{CdOH}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{CuO}$ ,  $\text{CuOH}^+$  and anions  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$  and proceeds into poral solution, pH of which is reduced to 4.0078, caused by high concentration of sulfuric acid anions (6.7259 mg/kg  $\text{H}_2\text{O}$  or mg/liter of water). Cadmium and copper ions amount in the resulting solution makes up respectively 1.125 and 0.635 mg/liter.

Much more ions of toxic metals (both in quantitative and qualitative terms) to aqueous solution produce selenides and tellurides. For example, computer modeling of oxidation of 1 mole tellurium-contained selenide of lead and bismuth (i.e., 652 g of mineral phase  $\text{Ag}_{0.3}\text{Cu}_{0.7}\text{Pb}_{0.5}\text{Bi}_{0.5}\text{As}_{0.5}\text{Sb}_{0.48}\text{Te}_{0.02}\text{Se}_{3.0}\text{S}_{1.0}$ ) with 1 ton of water equilibrated with the atmosphere show that because of this interaction, 114.38 g of  $\text{Bi}_2\text{O}_3$  (bismite), 140.67 g of  $\text{PbSO}_4$  (anglesite) and 80.87 g of  $\text{Sb}_2\text{O}_5$  (antimony oxide) are crystallized. But about half of primary minerals move into aqueous solution in form of following ions -  $\text{AgCO}_3^-$ ,  $\text{Ag}^+$ ,  $\text{AgNO}_3$ ,  $\text{AgOH}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{Bi}^{+3}$ ,  $\text{BiO}^+$ ,  $\text{BiO}_2^-$ ,  $\text{BiOH}^{+2}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{CuO}$ ,  $\text{CuOH}^+$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HSeO}_3$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{HBiO}_2$ ,  $\text{HSO}_4^-$ ,  $\text{HSeO}_4^-$ ,  $\text{Pb}^{+2}$ ,  $\text{PbCl}^+$ ,  $\text{PbCl}_2$ ,  $\text{PbOH}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ , the total concentration of which is 610.26 mg/liter of water. About 2/3 from these ions are anions of selenous, selenium, arsenic and sulfuric acid, which cause the increase of acidity of the resulting solution to  $\text{pH} = 4.1323$ . The toxic metal ions maximum concentrations (mg/liter) fall on  $\text{Cu}^{+2}$  (44.479),  $\text{Pb}^{+2}$  (7.432),  $\text{BiO}^+$  (1.726 or 1.61 translated on  $\text{Bi}^{+3}$ ),  $\text{H}_2\text{AsO}_4^-$  (69.38 or 37.46 translated on  $\text{As}^{+3}$ ),  $\text{HSeO}_3$  (383.92 or 238.03 translated on  $\text{Se}^{+6}$ ). Taking into account the values of maximum allowable concentrations (MAC) for natural river

waters, it is clearly visible that Cu concentration exceed MAC of 4447.9 times, Pb - 7432, Bi - 3.22, Ar - 749, and Se - 238030 times.

Thus, the results of computer modeling clearly show potential ecological hazard of hypergenic transformation of each ore mineral. However, the degree of toxic impact on the environment increases by several orders, if all natural associations of ore minerals are undergone hypergenic processes. The results of modeling of process of simultaneous hypergenic transformation of all ore minerals are good evidence for this. As a result of interaction of all ore minerals with 1 ton water equilibrated with the atmosphere, a few over half of primary mineral mixtures (approximately 55% of 11282 g) are transformed into secondary minerals - bismuth sulfate (2108.92 g of  $\text{Bi}_2(\text{SO}_4)_3$ ), hematite (229.15 g of  $\text{Fe}_2\text{O}_3$ ), anglesite (1831.51 g of  $\text{PbSO}_4$ ), biankite (1261.47 g of  $\text{ZnSO}_4(\text{H}_2\text{O})_6$ ), antimony oxide (1365.15 g of  $\text{Sb}_2\text{O}_5$ ) and hlorargirit (143.25 g of  $\text{AgCl}$ ). The remaining part of mineral mixtures come in aqueous solution in the form of various ions, total concentration of which is 10291.74 mg/liter of water. These ions are  $\text{AgCO}_3^-$ ,  $\text{Ag}^+$ ,  $\text{AgCl}$ ,  $\text{AgCl}_2^-$ ,  $\text{AgNO}_3$ ,  $\text{AgOH}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{Bi}^{+3}$ ,  $\text{BiO}^+$ ,  $\text{BiOH}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{CdCl}^+$ ,  $\text{CdCl}_2$ ,  $\text{CdOH}^+$ ,  $\text{Cl}^-$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{CuCl}^+$ ,  $\text{CuCl}_2$ ,  $\text{CuO}$ ,  $\text{CuOH}^+$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{FeCl}^{+2}$ ,  $\text{FeO}^+$ ,  $\text{FeOH}^{+2}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HSeO}_3$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{HBiO}_2$ ,  $\text{HSO}_4^-$ ,  $\text{HSeO}_4^-$ ,  $\text{Pb}^{+2}$ ,  $\text{PbCl}^+$ ,  $\text{PbCl}_2$ ,  $\text{PbOH}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ . The greatest amounts among these ions fall on (in mg/l)  $\text{Ag}^+$  (130.28),  $\text{AgNO}_3$  (224.96),  $\text{Cd}^{+2}$  (1.13),  $\text{Cu}^{+2}$  (2951.41),  $\text{H}_2\text{AsO}_4^-$  (920.02),  $\text{HSeO}_3$  (1074.59),  $\text{H}_3\text{AsO}_4$  (324.77),  $\text{HSO}_4^-$  (612.65),  $\text{Pb}^{+2}$  (0.14) и  $\text{SO}_4^{2-}$  (4012.23). Concentrations of ions  $\text{Ag}^+$ ,  $\text{Cd}^{+2}$ ,  $\text{Cu}^{+2}$  и  $\text{Pb}^{+2}$  exceed MAC for natural river waters respectively 2606, 226, 295141 and 140 times, and ions of arsenic and selenium translated onto  $\text{As}^{+3}$  и  $\text{Se}^{+6}$  respectively 666246 and 13195 times (see Fig. 1). It should be noted that high concentrations of anions of selenous, arsenic and sulfuric acids reduce pH of the aqueous solution to 2.6939, turning it into strongly acidic solution.

The degree of ecological hazard can be illustrated more tellingly by toxic elements amounts (in kg) that penetrate into the local hydrosphere for one year as a result of spontaneous migration from technogenic objects. For example, the content of  $\text{H}_2\text{AsO}_4^-$ , according to computer modeling is 920.02 mg/l, or 0.920 kg/ton of water. Taking into account annual rainfall in the deposit area (1000-1300 mm) and average area of tailings dam ( $60000 \text{ m}^2$ , i.e.  $200 \times 300 \text{ m}$ ), it is easy to calculate the amount of rain water which will fall on this area equal to 60000 tons. Correspondingly, the

$\text{H}_2\text{AsO}_4^-$  amount, which will be dissolved and take out by this volume of water will be about 55.2 tons. In terms of **pure arsenic it will be 29.26 tons** (arsenic makes 53% of  $\text{H}_2\text{AsO}_4^-$ ). Predictable amounts of other toxic elements that will penetrate into the local hydrosphere during year are calculated in the same way and make up (kg/year): **Pb - 81, Fe - 9630, Cd- 130, Cu - 177085, Bi - 302, Se - 39972, Sb - 85,  $\text{H}_2\text{SO}_4^-$  - 240734**. The results of realized modeling of physicochemical processes of transformation of the Prasolovka deposit ore minerals are fully verified by the data of geo-ecological research (hydrochemical study of drainage water and surface water) in the areas of concentration of mining and tailings dams (Bozhedomova, 2005 and many others).

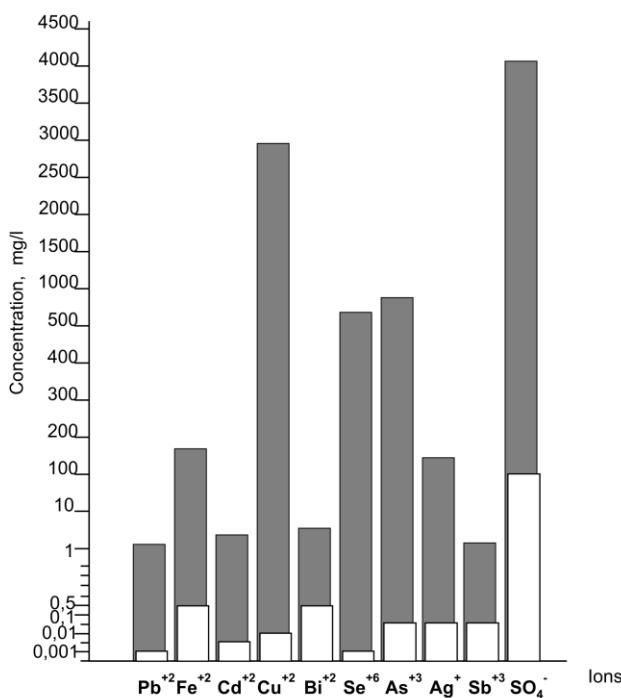


FIG. 1. THE TOXIC ELEMENTS CONCENTRATIONS RATIO

White - MAC for natural river waters, grey - concentration predictable in drainage waters as a result of hypergene transformation of ore minerals

## Conclusions

Thus, the results of computer modeling show that extracted and accumulated in tailing dam unclaimed ore mass represents a greatest ecological threat. Due to oxidation and dissolution of low quality ore mass

accumulated in tailings dam, some part of it are transformed into new mineral phases forming so-called secondary enrichment ores. However, about half of the primary ore mass, according to the results of modeling, passes into aqueous solution and by means of drainage water penetrating into local hydrosphere causing high concentrations of toxic elements. Getting into streams and rivers, toxic metals are included in trophic chain from plankton to zoobenthos and free-floating organisms and create a serious ecological threat to biosphere.

## ACKNOWLEDGMENT

This study was financially supported by Grant of President of the Russian Federation (No. 1159.2014.5) and Grant of Far Eastern Branch of the Russian Academy of Sciences (No. 12-3-A-08-150).

## REFERENCES

- Bozhedomova, S.A. "Environmental impact of mining on the environment of the East Kazakhstan region". Scientific and Educational Electronic Journal "Polysphere" 3 (2005). [in Russian]
- Horne, R. Marine Chemistry. Moscow: Mir, 1972. [in Russian].
- Jushkin, N.P., and Pavlishin, V.I. "Mineralogical problems of ecology". Mineralogical Magazine 2 (1991): 36-45. [in Russian].
- Karpov, I.K. Physico-chemical computer modeling in geochemistry. Novosibirsk: Nauka, 1981. [in Russian].
- Karpov, I.K., Kiselev, A.I., Letnikov, F.A. Modeling natural mineral on the computer. Moscow: Nedra, 1976. [in Russian].
- Kemkina, R.A., and Kemkin, I.V. Chemical composition of ores and mineralogo-geochemical methods of assessment of potential environmental contamination by toxic elements. Vladivostok: Dal'nauka, 2007. [in Russian].
- Trubetskoy, K.N., and Galchenko, Y.P. "Nature and man: the contradiction and ways to overcome them". Vestnik RAS 5 (2002): 405-409. [in Russian].